Magnetic susceptibility of 5·81 BM corresponded to 5 unpaired electrons in the complex indicating that iron in the complex is ionic and in the oxidation state +3. $K_3[Mn(CN)_5NO].2H_2O$ is diamagnetic. IR spectra and magnetic data, therefore, provide clear evidence that the nitro and the cyano groups are not involved in the reaction with Fe(III).

The Mössbauer spectra of the complex shows isomer shift of $0{\cdot}23 \pm 0{\cdot}02$ mm/sec and a quadrupole splitting of $0{\cdot}65 \pm 0{\cdot}02$ mm/sec. The value of isomer shift and quadrupole splitting show[12] that iron is ionic and in the trivalent state. The narrow line shapes show that Fe is only in one valency state, i.e. +3. The unusually large value of quadrupole splitting may be due to lattice distortion[13,14] around Fe ion as in the case of $FeCl_3.6H_2O$.

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Schiff Base Formation from Coordinated Diamine in Mixed Complexes of Cu(II) & Ni(II)

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Template synthesis of Schiff base complexes has been attempted by the reaction of salicylaldehyde with the mixed ligand complexes of the type [(L-L^{2-})M·1,3-diaminopropane], where L-LH_2 = catechol or 2,3-dihydroxynaphthalene. The resulting mixed complexes retain (L-L^{2-}) moiety in their structure and the —OH groups of the Schiff base N,N′-propylenebis(salicylaldimine) remain uncoordinated.

IN a recent communication[1] we have used the template method to react salicylaldehyde with ethylenediamine and propylenediamine in mixed ligand complexes of the type MAL where M = Cu(II) or Ni(II), A = catechol or 2,3-dihydroxynaphthalene and L = ethylene- or propylene-diamine. Two salicylaldehyde molecules undergo condensation with the two $-NH_2$ groups of the coordinated diamines and because of steric reasons the resultant complexes have a square-planar geometry where coordination occurs through the azomethine nitrogens and ligand A. It has been suggested earlier[2,3] that the Schiff base may occupy two equatorial and two axial positions if the length of the chain R in the diamine NH_2—R—NH_2 is more. As such the compounds of the type MAL where M = Cu(II) or Ni(II), A = catechol or 2,3-dihydroxynaphthalene and L = 1,3-diaminopropane have been prepared and their reactions with salicylaldehyde studied.

Methods of preparation — (i) Bis- or tris-(1,3-diaminopropane)nickel(II) chloride (0·5 g) was dissolved in the minimum quantity of water and aqueous solution of catechol (1*M*) added to it. The *p*H of the resultant solution was ~6. On trituration and leaving the solution aside for 30 min, a bluish green compound was obtained. It was washed with water, dried and analysed. (ii) To a mixture of equimolar (1*M*) aqueous solutions of nickel chloride and catechol in 1:2 ratio, an aqueous solution of 1,3-diaminopropane (1*M*) was added till *p*H was ~6. On trituration and leaving the solution aside for 30 min, a bluish green solid was obtained. It was washed with water, dried and analysed. The analysis of the compounds prepared by methods (i) and (ii) corresponds to the composition [Ni(cat)-(1,3-pn)].$2H_2O$. The same method was used for the preparation of [Cu(cat)(1,3-pn)].$2H_2O$. Similar mixed ligand complexes were also obtained when 2,3-dihydroxynaphthalene was used instead of catechol. The analytical results are shown in Table 1.

0·5 g of the diamine complex obtained above was reacted with 10 ml of salicylaldehyde. The mixture was refluxed on a water-bath for an hour. The solution was concentrated and excess of ether was added when a solid separated out. The compound in each case was washed with ether to remove excess of salicylaldehyde and recrystallized from chloroform. The compounds were found to be TLC pure (single spot). Co-TLC with Ni-SB indicated that the present complex is a mixed ligand complex of the type [MASB].

The magnetic susceptibilities of the isolated complexes were determined by Gouy's method.

The absorption spectra of the compounds I-IV (Table 1) have been studied in water and of the compounds V to VIII (Table 2) in chloroform. The spectra of the compounds were taken on a DU2 Beckman spectrophotometer at room temperature (30°), using 1 cm quartz cell in the range of 300-1000 nm.

The analysis of compounds I-IV shows them to be mixed ligand complexes. The water molecules are lost at 120°. These may be coordinated or may be water of crystallization.

The visible spectra of the Cu(II) complexes exhibit a broad band at ~650 nm. The Cu(II) complexes may have a square-planar structure. In

TABLE 1 — ANALYTICAL AND MAGNETIC MOMENT DATA OF THE MIXED LIGAND COMPLEXES

Complex	Metal (%)		N (%)		μeff.
	Calc.	Found	Calc.	Found	
[Ni(2,3-di-naph)(1,3-pn)].2H$_2$O (I)	17·96	17·60	8·56	8·42	2·95
[Ni(cat)(1,3-pn)].2H$_2$O (II)	21·20	20·96	10·10	9·95	3·02
[Cu(2,3-di-naph)(1,3-pn)].2H$_2$O (III)	19·15	19·00	8·44	8·55	1·79
[Cu(cat)(1,3-pn)].2H$_2$O (IV)	22·55	22·35	9·94	10·13	1·82

TABLE 2 — ANALYTICAL AND MAGNETIC MOMENT DATA OF SCHIFF BASE COMPLEXES

Complex	Metal (%)		N (%)		C (%)		H (%)		μeff.
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
[Ni(naph)(SB)*] (V)	11·76	11·60	5·61	5·64	64·96	64·36	4·81	4·60	Diamag.
[Ni(cat)(SB)*] (VI)	13·08	12·10	6·24	6·19	61·50	61·92	4·90	4·72	Diamag.
[Cu(naph)(SB)*] (VII)	12·61	12·60	5·55	5·50	64·33	64·75	4·76	4·46	1·82
[Cu(cat)(SB)*] (VIII)	14·00	13·96	6·17	6·09	60·84	60·92	4·84	4·72	1·80

*SB = N,N'-propylenebis(salicylaldimine).

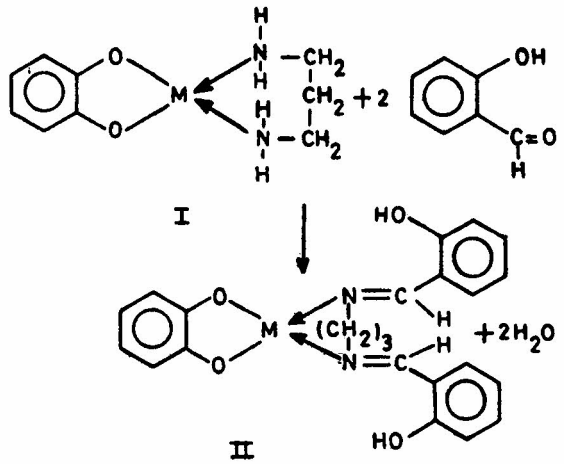
Ni(II) complexes there are shoulders at ~425 and ~500 nm and there is no band beyond ~600 nm. The absence of bands beyond ~600 nm indicates square-planar structure for Ni(II) complexes. The Cu(II) complexes are paramagnetic with magnetic moment equal to that due to one unpaired electron (~1·7 BM). The Ni(II) complexes are also found to be paramagnetic (~3·0 BM). The solid state paramagnetism of apparently four-coordinated Ni(II) complexes has been widely studied[4-6]. This can be attributed to polymerization in the solid state resulting in distorted octahedral structure[7]. Low solubility of the compounds in water and in organic solvents may support polymeric nature.

The absorption spectra were obtained in aqueous solution. In solution, the polymeric structure breaks giving the spectra corresponding to square-planar structure.

It is observed from the composition of the complexes V-VIII that catechol or 2,3-dihydroxynaphthalene are retained in the structure, and 1,3-diaminopropane in the original mixed ligand complexes (I) undergoes condensation with salicylaldehyde resulting in the formation of Schiff base complexes (II). The reaction can be shown as in Scheme 1.

The compounds are soluble in ethanol and chloroform. Their molar conductance in chloroform show that they are non-conducting. Ni(II) complexes are found to be diamagnetic. The Cu(II) complexes have magnetic moment values of ~1·8 BM. The absorption spectra of Ni(II) complexes exhibit shoulders at ~430 and ~520 nm. In case of Cu(II) complexes one band is observed ~550 nm.

In conformity with the earlier findings[1], catechol and 2,3-dihydroxynaphthalene remain coordinated in the Schiff base complexes and the hydroxy group of the salicylaldehyde remains uncoordinated.



Scheme 1

The IR spectra of the complexes V-VIII show a broad band in the region 3600-3200 cm^{-1} indicating the presence of uncoordinated OH group.

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